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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF ANIMAL INDUSTRY.—BULLETIN 124.

A. D. MELVIN, CHIEF OF BUREAU.

METHODS AND STANDARDS IN BOMB CALORIMETRY.

INVESTIGATIONS IN COOPERATION WITH THE INSTITUTE OF ANIMAL NUTRITION OF THE PENNSYLVANIA STATE COLLEGE.

UNIVERSITY OF CALIFORNIA AT LOS ANGELES
MAR 16 1938
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BY

J. AUGUST FRIES,
Assistant Expert in Animal Nutrition.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Animal Industry,
Washington, D. C., May 5, 1910.

Sir: I have the honor to transmit and to recommend for publication in the bulletin series of this Bureau a manuscript entitled "Methods and Standards in Bomb Calorimetry," by J. August Fries, assistant expert in animal nutrition.

The investigation described is a continuation of that already reported in Bulletin 94 of this Bureau, and is connected with the work in animal nutrition conducted at State College, Pa., by cooperation between the institute of animal nutrition of the Pennsylvania State College and this Bureau through its Animal Husbandry Division. The particular objects sought to be attained by Mr. Fries in the present paper are set forth in the accompanying letter of Doctor Armsby, the expert in direct charge of the cooperative investigations.

Respectfully,

A. D. Melvin,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

LETTER OF SUBMITTAL.

STATE COLLEGE, PA., *October 20, 1909.*

SIR: I have the honor to submit herewith the results of experiments by Mr. J. August Fries, M. S., assistant expert in animal nutrition, upon "Methods and Standards in Bomb Calorimetry."

The accurate determination of the heats of combustion of organic substances is not only a fundamental requirement in the nutrition investigations now being conducted in cooperation with the institute of animal nutrition of the Pennsylvania State College, but is of great importance in many other lines of both scientific and technological research. Mr. Fries's investigations are a continuation of those reported in Bulletin 94 of the Bureau of Animal Industry and deal essentially with the standardization of methods as a means of securing results which shall be comparable among themselves and bear a definite relation to established physical constants. To this end a new method of determining the hydrothermal equivalent of the bomb calorimeter has been devised; the influence of impurities in the oxygen used, as well as of some other minor sources of error, has been studied; and a redetermination of the heat of combustion of benzoic acid has been made with reference to its acceptance as a standard substance in bomb calorimetry.

It is believed that the results of these investigations will be of interest and value to all experimenters who use the bomb calorimeter for any purpose.

Very respectfully, HENRY PRENTISS ARMSBY,
Expert in Animal Nutrition.

Dr. A. D. MELVIN,
Chief of the Bureau of Animal Industry.

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METHODS AND STANDARDS IN BOMB CALORIMETRY.

INTRODUCTION.

The bomb calorimeter not only is coming more and more into use in research and instruction laboratories, but has also found large practical application in fuel-testing laboratories, and is beginning to find a place of usefulness as a method of chemical analysis. With this increase in bomb-calorimeter work, and consequently increased publication of results, one fact has been brought out very clearly, namely, that there is at present great lack of uniformity in the work. Reports of the work done in these various kinds of laboratories, by differently trained men using different types of bomb calorimeters, seem to indicate that calorimetry, instead of becoming more perfected and reliable by wider application, is in a sense becoming more chaotic. One man's work can not readily be compared with that of another. A calorie, in other words, is not a definite fixed quantity, as it should be in bomb-calorimeter work, since no two persons necessarily agree concerning what standard to use.

HYDROTHERMAL EQUIVALENT OF THE CALORIMETER.

Each individual bomb calorimeter must have its hydrothermal equivalent, or water value, determined; that is, the number of calories required to raise the mass of water and metal one degree Centigrade. Preferably, this should be done at the place where it is to be used, and by the individual who is to be responsible for the work. For this purpose it is customary to burn substances—like benzoic acid, naphthalin, camphor, cellulose, sugar, etc.—of known chemical composition, which as a rule burn readily, can easily be obtained in a high state of purity, and whose heats of combustion are supposed to be known. As to the choice of a substance against which to standardize the apparatus, however, the investigators or operators do not agree, each selecting according to his own fancy and convenience, or as influenced by some one else. Thus, some may use several substances while others choose only one. One set of analysts use naphthalin and give it a heat value of 9,628 calories per gram, while others using the same substance give it a heat value of 9,696 calories per gram. Some use benzoic acid, accepting 6,322 calories per gram as its heat of combustion value, while others regard this as too low, and

use 6,335 or some other number of calories as the correct value for the standard on which their work is based. Such cases could be multiplied. Each man for himself, apparently, is the condition.

NECESSITY OF A COMMON STANDARD.

Now, if work of this nature is to reach its greatest usefulness—that is, if the work of each individual is to be relied upon to mean a definite thing and thus be of use to everybody else interested in the same line of work—then we need above all things one common standard. The writer believes that it is high time that some single substance be chosen, a heat value agreed upon, and that substance in some way recognized as a standard for bomb-calorimeter work. In the future, should the heat value of such a substance have to be slightly changed, results would still be useful and comparable after a little calculation.

From his own personal experience with the substances mentioned, the writer believes that benzoic acid meets the requirements for a standard better than any of the other substances, and considers it the most suitable that could be selected for such a standard. It was, therefore, for the purpose of calling attention to existing conditions and with the hope of perchance being able to do something which should help to bring to pass in the near future the adoption of such a standard that a redetermination of the heat of combustion of benzoic acid was undertaken.

The plan of the undertaking was to determine again the heat of combustion of benzoic acid, independently of all previous determinations of the heat of combustion of any organic substance whatsoever, using an improved bomb. calorimeter recently described.[a] The problem itself, which it was desired to work out step by step, with reference to the material and apparatus on hand, can be stated as follows:

Having a new bomb calorimeter of unknown hydrothermal equivalent, or water value, also an oxygen supply of undetermined correction for any combustible gases which may be present as impurity, and assuming that no organic substance exists which has had its heat of combustion accurately determined so as to be referred to or accepted as a standard; to determine the heat of combustion of benzoic acid.

DETERMINATION OF THE WATER VALUE OF THE BOMB CALORIMETER.

The first requirement in order to solve the problem before us is to determine the water equivalent of the whole bomb-calorimeter system, assuming also that no substance with a known heat of combustion value was to be had. In order to determine this water value of

[a] The Journal of the American Chemical Society, Vol. XXI, p. 272, 1909.

the apparatus two known methods, one of which at least is frequently referred to in connection with the bomb calorimeter, were used, and also a third method devised by the writer.

BY COMPUTATION OF COMPONENT PARTS.

The first and more commonly used of the two known methods consists in computing from the weight of each of the component parts of the bomb system and the corresponding specific heats the water value of each substance, the sum of all giving the water equivalent of the whole system or apparatus. This method is not necessarily absolutely correct, since the weight of some of the parts can only be known approximately, as, for instance, the glass and mercury of the thermometer, small rubber pieces, etc., which can not be disconnected or weighed. Further, the specific heat of the particular steel used for the bomb itself has not been determined, nor is it certain that the other specific heats are all absolutely correct. However, while we can not claim absolute correctness for this method, the total value obtained for the whole system, including the water, need not vary more than a few hundredths, or at most a very few tenths, of 1 per cent from the true water value.

The apparatus in question was an Atwater-Hempel bomb calorimeter, having the top modified so as to permit the determination of the carbon dioxid after a combustion. The modification consists in having, besides the usual valve and opening for the intake of oxygen, an outlet terminating in a platinum tube near the bottom of the bomb and through which the gases are removed for analysis.

From the weight of each of its different parts and their respective specific heats, the following water value for the bomb calorimeter system was obtained:

TABLE 1.—*Computed water value of bomb calorimeter.*

Material.	Weight.	Specific heats.	Water equivalent.
	Grams.		*Grams.*
Steel	3,236.0	[a] 0.1114	360.49
Platinum	196.0	[a].0320	6.27
Lead	66.0	[a].0300	1.98
German silver (approximate)	4.0	[a].0940	0.38
Rubber (approximate)	4.0	[b].3310	1.32
Iron (approximate)	10.0	[a].1114	1.11
Mercury (approximate)	50.0	[a].0330	1.65
Glass (approximate)	10.0	[a].1900	1.90
Britannia metal	855.0	[a].0548	46.85
Oxygen (constant volume)	11.4	[a].1570	1.79
Water at 22° C	2,000.0	[c].9975	1,995.00
Total			2,418.74

[a] The Journal of the American Chemical Society. Vol. XXV, p. 694. 1903.
[b] H. W. Wiley. Principles and Practice of Agricultural Analysis. Vol. III, p. 573. 1897.
[c] Annalen der Physik. ser. 4, **16**, 616 (1905.)

Except in the cases of rubber and water, the specific heats used in the above computation are those used by Atwater in determining the water value of his bomb calorimeter. For the small quantity of iron in the connectors the same specific heat is used as for the steel. The specific heat of water is the average result of Dieterici and Barnes's determinations.

According to Table 1, the total water equivalent of the whole bomb-calorimeter system, including the water, is 2,418.74, or without the water it is 423.74. Should the other value given by Atwater for steel (0.1087 specific heat) be used, the water equivalent would be 415, or 2,410 including the water. The water in which the bomb is immersed and through which the heat is measured should always be the same in amount in order to insure the same water level in the cylinder, thus keeping the conditions unchanged. With this apparatus 2,000 grams of water will immerse the bomb completely, and is the quantity which was uniformly employed.

THE ELECTRIC METHOD.

The second method employed in determining the water equivalent consisted in generating a measured amount of heat in the bomb by means of an electric current passing through a resistance coil. The generation of heat in the bomb and the measurement of the rise in temperature due to it were done under the same conditions as when a substance is burned for its energy determination, except that no oxygen was introduced into the bomb. Correction, therefore, must be made for the usual amount of oxygen in computing the results.

The test was made in the following manner: About 10 inches of size 26 B. & S. = 0.016 "nichrome" resistance wire was made into a small coil which was connected to the two platinum wires in the bomb in such a manner that the heat would be generated at about the same place as where the substances analyzed are burned. The resistance of this wire coil was about 1.38 ohms. Next, the bomb was closed, placed in the water, and connected up as for a determination of heat of combustion, and the two insulated copper wires leading from the bomb were connected to the electrical instrument. The electric current was supplied by six storage cells and was measured by voltmeter and ammeter. After starting the stirrer and taking the usual few minutes preliminary readings of the water temperatures, the switch was closed at a given signal and the current from the six cells sent through the bomb. It was allowed to flow through for a number of minutes, the readings of the voltmeter and ammeter being taken every half minute. The water temperature was taken every minute by means of a Beckman thermometer read to 0.001° C. During the first few trials the voltmeter and ammeter used were the

commercial, so-called American, instruments, the ammeter having an external shunt.

The various observations noted during one of these trials in which the electric current was on continuously for 12 minutes are found in Table 2.

TABLE 2.—*Electric determination of water equivalent.*

Period.	Time.	Temperature of calorimeter.		Voltmeter.	Ammeter.
		As read.	Corrected.		
	Minutes.	° *C.*	° *C.*	*Volts.*	*Amperes.*
Preliminary	1.0	1.236	1.2432	.....	.....
	2.0	1.239	.....	.....	.....
	3.0	1.244	.....	.....	.....
	4.0	1.247	.....	.....	.....
	5.0	1.252	1.2592	.....	.....
Current on	5.5	.....	.....	11.68	4.62
	6.0	1.370	1.3781	11.62	4.60
	6.5	.....	.....	11.60	4.60
	7.0	1.660	1.6696	11.60	4.60
	7.5	.....	.....	11.59	4.58
	8.0	1.970	1.9807	11.59	4.58
	8.5	.....	.....	11.58	4.58
	9.0	2.280	2.2918	11.58	4.58
	9.5	.....	.....	11.58	4.60
	10.0	2.595	2.6084	11.58	4.60
	10.5	.....	.....	11.58	4.60
	11.0	2.910	2.9240	11.58	4.60
	11.5	.....	.....	11.58	4.60
	12.0	3.225	3.2385	11.58	4.60
	12.5	.....	.....	11.58	4.60
	13.0	3.545	3.5567	11.58	4.60
	13.5	.....	.....	11.58	4.60
	14.0	3.845	3.8564	11.58	4.60
	14.5	.....	.....	11.58	4.60
	15.0	4.155	4.1667	11.58	4.60
	15.5	.....	.....	11.58	4.60
	16.0	4.470	4.4816	11.58	4.60
	16.5	.....	.....	11.58	4.60
	17.0	4.780	4.7914	11.58	4.60
Equalizing	18.0	4.974	4.9860	.....	.....
	19.0	5.005	5.0170	.....	.....
	20.0	5.008	5.0200	.....	.....
	21.0	5.009	5.0210	.....	.....
End period	22.0	5.006	.....	.....	.....
	23.0	5.004	.....	.....	.....
	24.0	5.001	.....	.....	.....
	25.0	4.998	5.0100	.....	.....

The ammeter used had an initial correction of 0.16, which has to be added to the average of the readings. Accordingly, the average for the current was:

For total time, 11.588 volts, 4.757 amperes; for last 8 minutes, 11.58 volts, 4.76 amperes.
Room temperature, 24° C.
Temperature of water at beginning, 21.2° C.
Temperature of water at end, 25.0° C

Most of the figures found in the second column of Table 2 were read when the mercury column in the thermometer was moving rather fast, hence a ± error of one or two thousandths of a degree could readily be made, but any error of that kind is reduced to a

minimum by the number of readings taken. If we examine the table, we notice that from about the third minute there was a uniform increase in temperature of the bomb system, while the voltmeter and ammeter remained unchanged, indicating a constant current. Because of this constancy, as regards both the current and the rise in temperature of the calorimeter, the results of the test can be worked out either from the total rise in temperature and total heat generated, or from a section of the time consisting of the last 8 or 9 minutes.

The radiation correction, or correction due to the influence of the surrounding air conditions, in the case of the electric tests, as well as in all the following determinations of heats of combustion, has been worked out by using the Regnault-Pfaundler formula [a]—

$$\frac{v-v'}{t'-t}\left(\sum_1^{n-1}\theta r+\frac{\theta n+\theta_1}{2}-nt\right)-(n-1)v=\Sigma\Delta t$$

$\sum_1^{n-1}\theta r$ = sum of readings minus 1 increased by an arbitrary factor $\frac{\theta_2-\theta_1}{9}$

v = average rate of radiation during preliminary period.

v' = average rate of radiation during end period.

θn = number of readings during combustion period.

t = average of preliminary thermometer readings.

t' = average of end period thermometer readings.

Applying the correction thus found to the entire test represented by Table 2, we have:

	°C
Last reading of the heating period	+5.0210
First reading of the heating period	−1.2592
Radiation correction	− .0029
Correction for thermometer lag	− .0010
Total rise in temperature	3.7579

If we take a section consisting of the last 8 minutes of the test, and represent by means of a curve the gain and loss to the system by radiation, we obtain a correction of +0.0013° C. and a correction for thermometer lag of −0.0005° C. Applying these corrections to the last 8 minutes, we have:

	°C
Thermometer reading for the twelfth minute	+4.7914
Thermometer reading for the fourth minute	−2.2918
Radiation correction	+ .0013
Correction for thermometer lag	− .0005
Corrected rise for 8 minutes	2.5004

In computing the heat generated in the bomb by the electric current and the corresponding water equivalent of the apparatus the

[a] H. W. Wiley. Principles and Practice of Agricultural Analysis. 1897. Vol. III, p. 572.

mean small calorie is used, that is, one one-hundredth of the heat required to heat 1 gram of water from 0° to 100° C., equivalent to 4.1834 Joules.[a] The electrical energy developed in the bomb and measured as heat would then be expressed in calories by the following formula:

$$\text{Calories} = \frac{\text{volts} \times \text{amperes} \times \text{seconds}}{4.1834}$$

During the 12 minutes, or 720 seconds, we had the following amount of heat evolved in the bomb:

$11.588 \times 4.757 \times 720 \div 4.1834 = 9{,}487.4$ calories,

and

9,487.4 calories $\div$ 3.7579° rise = 2,524.7 grams water equivalent.

At the time of the test there was no oxygen in the bomb; hence a correction for the amount usually present in the bomb must be applied. The amount of oxygen in this bomb at 20 atmospheres pressure equals 10.24 grams, which, multiplied by 0.157—the specific heat of oxygen at constant volume—equals 1.6 grams water, which must be added to the results found for the whole system, giving $2{,}524.7 + 1.6 = 2{,}526.3$ grams as the water equivalent.

For the 8-minute section referred to we have:

$11.580 \times 4.76 \times 480 \div 4.1834 = 6{,}324.5$ calories,

and

$6{,}324.5 \div 2.5004 = 2{,}529.3$ grams. Adding 1.6 for the oxygen to it gives a water equivalent of 2,530.9.

Two other tests with the same instruments were made, one having the current on for 10 minutes and the other for 12 minutes, and worked out in the manner already described, the results of the three tests being given in Table 3 below.

TABLE 3.—*Water equivalent of calorimeter by three electric tests.*

Test.	Time.	Heat evolved in the bomb.	Corrected rise in temperature.	Water equivalent.	Correction for O_2.	Water equivalent corrected.
		Calories.	*° C.*	*Grams.*	*Grams.*	*Grams.*
1	Total 12 minutes	9,487.4	3.7579	2,524.7	1.6	2,526.3
	Last 8 minutes	6,324.5	2.5004	2,529.3	1.6	2,530.9
2	Total 10 minutes	7,969.6	3.1374	2,540.1	1.6	2,541.7
	Last 6 minutes	4,759.2	1.8885	2,520.1	1.6	2,521.7
3	Total 12 minutes	9,486.9	3.7603	2,522.9	1.6	2,524.5
	Last 8 minutes	6,313.0	2.4910	2,534.3	1.6	2,535.9

The average water value of the three tests obtained when the total heat is used is equivalent to 2,530.8 grams of water, and when the effect of the last 8 and 6 minutes of the electric current is considered, the average water value is equal to 2,529.5 grams.

[a] A. W. Smith. Monthly Weather Review for October, 1907, p. 11.

These results are about 4.6 per cent higher than that calculated from the weights and specific heats of the material of the bomb. Among themselves, the results agree fairly well, an indication that the source of error, if any exists, must be a constant one. Suspicion fell upon the ammeter, which already had an initial error of +0.16 ampere, and the possibility of electrolytic action upon the water. Another ammeter was used, this time a Weston instrument, and a piece of rubber tubing was slipped over the metal connector so as to have no metal in direct contact with the water. Two tests were made under these conditions, the electric current being on for 12 minutes in each case.

Without reproducing the readings of the instruments, etc., the total heat as well as the heat evolved in the bomb during the last 9 minutes, the corresponding rise in temperature, and the water equivalent of the bomb system are shown in Table 4.

TABLE 4.—*Water equivalent of calorimeter by two electric tests.*

Test.	Time.	Heat evolved in the bomb.	Corrected rise in temperature.	Water equivalent.	Correction for O_2.	Water equivalent corrected.
		Calories.	*°C.*	*Grams.*	*Grams.*	*Grams.*
1	Total 12 minutes	9,125.5	3.6985	2,467.3	1.6	2,468.9
	Last 9 minutes	6,828.7	2.7550	2,478.6	1.6	2,480.2
2	Total 12 minutes	9,066.1	3.6710	2,469.6	1.6	2,471.2
	Last 9 minutes	6,790.5	2.7445	2,474.2	1.6	2,475.8

With instruments of this kind where the hundredth part of an ampere or volt has to be estimated it can not be claimed nor expected that the results should be reliable to within ±0.5 per cent. The average of the above water equivalents equals 2,474 grams, which is still over 2 per cent above that computed from the specific heats. It was therefore decided to test one more possible source of error, viz, the evaporation of water from the system under the existing laboratory conditions.

ERROR DUE TO EVAPORATION OF WATER.

The evaporation from the surface of the water in the cylinder containing the bomb is held to be of so little consequence that it is generally entirely neglected, but the writer made a few tests in order to get results which should apply to this apparatus, locality, and laboratory. In the Atwater-Hempel bomb calorimeter the water cylinder is surrounded by two separate dead-air spaces, and the two covers for these spaces are of smooth hard rubber. These covers fit snugly, so that practically there can be no currents in the inclosed air.

The tests were made in the following manner: The water cylinder was filled with water to the same level as when the bomb is in place. The stirrer was placed in the water, and to represent the two rubber-

covered connecting wires for the electric current, two similar small pieces of rubber-covered wire were suspended from the edge of the vessel dipping into the water. The cylinder was then weighed to 0.01 gram and the exact time noted. It was then quickly put in its place and the stirrer operated as during a combustion for from 15 to 30 minutes. The time of starting and stopping the stirrer, as well as the time of weighing, was noted.

These evaporation tests were carried on in the calorimeter both with the stirrer in operation and with the stirrer standing undisturbed, but covered. The water was also left standing exposed to the air of the laboratory in a place where there was no draft. Standing exposed in the laboratory, the average of several trials was 0.0193 gram of water evaporated per minute, whereas standing covered in the bomb calorimeter the evaporation was only 0.0034 gram per minute. When the stirrer was in operation, the evaporation increased. Below are given the details of one of the trials:

TABLE 5.—*Evaporation of water from calorimeter.*

Items.	Time.	Weight of vessel + water, stirrer, etc.
		Grams.
Stirrer started	9.40 a. m.	
Stirrer stopped	10.10 a. m.	
Difference	30 minutes	
Weight before taken	9.38 a. m.	3,600.56
Weight after taken	10.13 a. m.	3,600.12
Difference	35 minutes	.44

Temperature of room, 21° C.
Temperature of water, 21° C.
Time of stirring the water, 30 minutes.
Time required for handling, 5 minutes.
Correction for 5 minutes, $5 \times 0.0193 = 0.097$ gram H_2O.
$0.44 - 0.097 = 0.343$ gram evaporated during 30 minutes, or 0.0114 gram per minute.

Ten trials showed the following rates of evaporation per minute:

	Gram.
No. 1	0.0067
No. 2	.0113
No. 3	.0075
No. 4	.0122
No. 5	.0114
No. 6	.0085
No. 7	.0107
No. 8	.0044
No. 9	.0048
No. 10	.0075
Average	.0085

These tests were made between November 30 and January 17.

The above evaporation, though small, makes a correction which should not be neglected, especially when small charges are used, or charges in any way differing from the quantity used in the standardization of the apparatus. The heat of water at 21° C. is, according to Prof. A. W. Smith,[a] equal to 585.26 mean calories for 1 gram of water.

If we apply the above correction to the last-mentioned electric tests (Table 4) it would be 16[b] minutes $\times 0.008$ gram $H_2O = 0.128$ gram H_2O and $0.128 \times 585.26 = 74.93$ calories to be subtracted from the calories given in the first column opposite the total for 12 minutes. For the 9 minutes section the correction would be $9 \times 0.008 = 0.072$ gram H_2O, and $0.072 \times 585.26 = 42.14$ calories. Recalculating, the four water values would be:

2,447.09
2,463.36
2,449.24
2,458.87

Average=2,454.64

This corrected average water value is still over 1.3 per cent greater than that computed according to the first method, and the difference is undoubtedly too large to be ascribed to the manipulation or reading of the instrument. In all probability some electrolysis of water must have taken place in spite of the precaution taken, and we can not be sure on this point, since the connection was not dry. Any error due to condensation of moisture on the outside of the water vessel, and subsequent evaporation of the same, has not been observed and can at best be but small.

The evaporation tests may throw some light upon this problem of condensation, etc. The inner air space or layer of air which surrounds the water cylinder in the calorimeter equals about 4 liters. At 22° C. these 4 liters of air when saturated would contain 0.0772 gram of water. In about 9 minutes, therefore, perfectly dry air should become fully saturated and the evaporation cease. This is not the case. The tests showed that the evaporation continued unchecked, and in the particular test already referred to there was a loss of 0.343 gram of water in 30 minutes, enough water to saturate 17.8 liters of dry air. But since the air in the calorimeter laboratory always contains some moisture, in reality a much larger volume of air would be saturated. The fiber envelope is supposed to be waterproof, and hence it is very unlikely that the water vapor is absorbed. It would seem that the water vapor which is produced at the surface of the water, near the cover, escapes to the outside by means of its

[a] Physical Review, Vol. XXV, No. 3, Sept., 1907, p. 170.

[b] This refers to the total time influenced by the evaporation of water when the total heat generated during the full time of 12 minutes is considered.

own pressure through the openings in and around the cover. This unchecked evaporation and free escape of the vapor seems to indicate that the inclosed air need not necessarily be affected much, except at the very top, and that the air layer around the water cylinder is slowly changed by diffusion and convection currents.

A direct test, by a wet and a dry bulb thermometer, which were 6.0° C. apart when standing quietly in the laboratory, showed that there was no effect whatever upon the moisture conditions in the air space during 10 minutes' operation of the bomb. These thermometers, bulbs one-third down in the space, stood 3.0° C. apart and remained so; hence there could be no condensation of moisture on the sides of the vessel.

If, now, the water cylinder as it is placed in position is a little (say 0.5 to 1° C.) colder than the air surrounding it, and the air is saturated with moisture, condensation would begin, but the conditions in the bomb room have never at the time of making a combustion been such that a condensation would have taken place at the start with only one degree difference in temperature. The water cylinder is in the calorimeter only a few minutes, as a rule, before the substance is ignited, and it is questionable if in that length of time the conditions of the air have changed enough so that a condensation can take place, except, perhaps, at the upper rim of the vessel. In less than a minute after ignition, the temperature of the water is higher than that of the surrounding air, and hence evaporation of any water which had been condensed on the vessel before the ignition took place would begin. Whether any condensation or evaporation does take place has not been experimentally demonstrated, but from the very nature of the existing conditions at this place, errors due to them may be assumed to be entirely negligible.

As a check on these evaporation results, on a clear bright day a special test was made as follows: The water cylinder, filled with water to within one-half inch of the top, was placed in position in the calorimeter container, as during an energy determination, but without the stirrer. The covers were put on as before and the cylinder was allowed to stand for 20 minutes. It was taken out and reweighed quickly, and put back the second time for 20 minutes. After that it was allowed to stand in the laboratory for 24 minutes before being weighed, another weight being taken 8 minutes later. During this laboratory test the windows and doors were closed so that there was no draft to influence the evaporation. Next, a piece of paraffined paper was fitted over the top of the water cylinder and sealed by means of melted soft wax. The cylinder was weighed and put in position in the calorimeter container as before and reweighed after 20 minutes. After that it was allowed to stand in the laboratory and

was weighed after different intervals. The results are as given in Table 6.

TABLE 6.—*Evaporation tests.*

Method.	Water cylinder.			Evaporation per minute.	
	Time weighed.	Weight.	Time placed in position and removed.	In laboratory.	In bomb room.
CYLINDER UNCOVERED.		*Grams.*		*Gram* H_2O.	*Gram* H_2O.
Bomb room, first trial	9.14 a. m. 9.36½ a. m.	3,480.43 3,480.32	9.15 a. m. 9.35 a. m.		
Difference	22½ mins.	.11	20 mins.		
Bomb room, second trial	9.36½ a. m. 9.58 a. m.	3,480.32 3,480.21	9.37¼ a. m. 9.57¼ a. m.		
Difference	21½ mins.	.11	20 mins.		
Average					0.0035
Laboratory, first trial	9.58 a. m. 10.22 a. m.	3,480.21 3,479.71			
Difference	24 mins.	.50			
Laboratory, second trial	10.22 a. m. 10.30 a. m.	3,479.71 3,479.58			
Difference	8 mins.	.13			
Average				0.0197	
CYLINDER SEALED.					
Bomb room	10.37 a. m. 10.59 a. m.	3,483.86 3,483.86			
Difference	22 mins.	0.00		0.0000	
Laboratory, first trial	10.59 a. m. 11.29 a. m.	3,483.86 3,483.86			
Difference	30 mins.	0.00			
Laboratory, second trial	11.29 a. m. 2.46 p. m.	3,483.86 3,483.87			
Difference	197 mins.	+.01			
Average					0.0000

From this test we see that the change in weight of the water cylinder in the previous tests was due entirely to evaporation from the surface of the liquid water, and that there was no condensation on the sides of the cylinder or evaporation of any condensed moisture. During the test the temperature of the bomb room was 24° C., and the wet-bulb thermometer (having the bulb surrounded by a piece of moistened filter paper and swung back and forth) registered 16° C. The temperature of the water was 24° C., and in the laboratory the dry thermometer registered 26.5° C., and the wet-bulb thermometer 16° C.

The water equivalent of the bomb as determined by the electrical tests which have been described is not satisfactory, but the tests

have, nevertheless, been useful and seem to justify the following conclusions:

1. The tendency of the electric method is to give results that are too high.

2. There are many chances for error connected with an electric test, even if the instruments used have been carefully calibrated.

3. Instruments which can be read to the hundredth part of an ampere and volt only by estimation are not accurate enough for the best work.

4. There is a possibility of electrolysis of water; hence the connection to the one wire in the bomb should not only be insulated from the metal of the bomb, but thoroughly insulated from the water surrounding the bomb as well.

5. The tests led to a more thorough investigation of the error due to evaporation of water during a bomb combustion, showing that under usual laboratory conditions there is an error which must be taken into account, at least when less or more heat is generated in the bomb than was generated at the time of its standardization.

A THIRD METHOD.

The uncertainty of the foregoing results prompted the working out of a simple and perfectly reliable method for the determination of the water equivalent of the calorimeter.

The principle of this method consists in burning equal charges of a substance in the bomb, first, under exactly the same conditions as when a heat determination is made, and, secondly, after having, without changing any of the external conditions, such as level of water, etc., reduced the water equivalent of the system. The same amount of oxygen is used in each case. From the difference in rise of temperature and the difference in water equivalent it is possible to determine very accurately the water value of the calorimeter.

By this method it is possible, first, to use a substance of unknown or only approximately known heat of combustion and an oxygen supply of unknown purity to determine the water equivalent of the apparatus, and then by means of this new water equivalent and the same determinations to work out accurately the heat of combustion of the substance used, and also to determine the correction for impurities in the oxygen, if any such were present.

DISPLACEMENT OF WATER.

When the bomb and stirrer are in position in the water cylinder, there is a space above the bomb and one near the bottom where part of the water can be displaced, and thereby the water equivalent of the system reduced. The displacement of water was effected by two

double-walled metal rings. The one to fit above the bomb was made of sheet lead heavy enough to rest securely by its own weight. The one for near the bottom of the bomb was made of sheet zinc and was held in position by the bomb itself, hence it could be lighter than the water displaced. These rings were so made that they did not touch the sides of the water cylinder or in any way interfere with the operation of the stirrer or the thorough mixing of the water. The upper and heavier ring contained 553.5 grams of lead and solder and 25.8 grams of zinc, and had a displacement of 306 grams of water. The lower ring contained 86 grams of zinc and 20.9 grams of solder and had a displacement of 162 grams of water.

The computed water equivalent of the metal rings was:

Lead (+solder) 574.4 grams×0.0315 sp. heat [a]	=18.09
Zinc 111.8 grams×0.0956 sp. heat [a]	=10.68
Total	28.77

During a heat of combustion determination the bomb is immersed in 2,000 grams of water, which covers the highest point of the bomb to a certain depth. When the metal rings were used, a quantity of 1,532 grams of water brought the water level to this same height. To these 1,532 grams of water must be added the 28.8 grams water equivalent of the metal. Thus we have a difference of 2,000 grams $-1{,}560.8 = 439.2$ grams of H_2O, or $439.2 \times 0.99745 = 438.1$, in the water equivalent of the calorimeter at 22.12° C., the temperature at which the determinations of water value were made, without changing any of the other conditions. If, now, exactly equal weights of a substance and fuse wire are burned, that is, if the same amount of heat is generated in the bomb while it is immersed in the two different quantities of water, there will be a difference in the rise of temperature, and we have the necessary factors for the computation of the water value.

It is, however, a tedious and difficult manipulation to press and weigh out to the accuracy of 0.0001 gram a charge of dry, and perhaps hygroscopic material, and it is much more convenient and just as accurate to weigh out approximately equal quantities of the substance for each charge, and then, by one or the other of the two methods of calculation to be described, to compute the water equivalent of the apparatus.

In the following table (Table 7) are shown the results of a number of combustions of about equal charges of benzoic acid made under the two conditions, representing a difference of 439.2 grams of water, equal to 438.1 grams water equivalent of the system at 22° C.

[a] Beilage zum Chemiker Kalender, 1904.

TABLE 7.—*Rise in temperature due to burning like quantities of benzoic acid in the bomb, with 20 atmospheres oxygen pressure, but with varying amounts of water in the apparatus, there being a difference of 439.2 grams of water equal to 438.1 water equivalent.*

Water used.	Benzoic acid burned.	Fuse wire.	HNO_3 formed.	Rise in temperature (not corrected for evaporation or impurities in oxygen).	Rise in temperature due to wire and HNO_3.	Rise due to benzoic acid.	Rise due to 1 gram of benzoic acid.
Grams.	*Gram.*	*Calories.*	*Calories.*	° *C.*	° *C.*	° *C.*	° *C.*
2,000.....	0.7157	26.24	7.10	1.8837	0.01378	1.86992	2.61272
2,000.....	.7341	22.88	7.20	1.9293	.01244	1.91686	2.61117
2,000.....	.7034	26.24	6.90	1.8476	.01370	1.83390	2.60719
2,000.....	.7162	23.04	6.95	1.8826	.01240	1.87020	2.61128
2,000.....	.7110	26.56	6.95	1.8726	.01386	1.85874	2.61426
2,000.....	.7045	23.68	6.95	1.8510	.01266	1.83834	2.60943
Average.....							2.61101
1,560.8.....	.7122	26.24	8.25	2.2937	.01741	2.27629	3.19614
1,560.8.....	.6990	26.24	7.15	2.2467	.01686	2.22984	3.19004
1,560.8.....	.7031	26.24	7.40	2.2606	.01698	2.24362	3.19104
1,560.8.....	.7028	26.24	7.85	2.2524	.01721	2.23519	3.18041
Average.....							3.18941

Difference in rise of temperature, 0.57840° C.

WATER VALUE OF THE CALORIMETER.

Two methods can be employed to compute the water equivalent of the apparatus from the above determinations.

One method is to make use of the approximate heat of combustion value of benzoic acid, compute the total heat generated by each charge, the fuse wire, and the nitric acid, and from the average difference in rise of temperature due to a given difference in the water equivalent of the calorimeter to compute the water equivalent of the apparatus. The approximate heat of combustion value of the substance burned is computed from the combustions made under normal conditions, using the computed water value for the calorimeter, i. e., 2,418.74 grams. The approximate heat of combustion of benzoic acid computed in this way would be 6,315.3 calories per gram.

The second method consists in finding the value of the number of calories represented by the fuse wire and the nitric acid of each charge in terms of degrees rise in temperature, subtracting this from the observed rise in temperature, and then expressing the rise in temperature as per gram substance burned. The water equivalent of the apparatus is calculated from the average difference in the rise of temperature per gram and the difference between the two water equivalents. This method of computing is perhaps preferable to the former, and since the corrections for the wire and the nitric acid are small at best, it may be more correct in case there should be much variation in the size of the charges used for combustion. In Table 7 the rise per 1 gram of the substance has been obtained according to this

method. To find the rise of temperature of the calorimeter due to the burning of the wire and formation of HNO_3, we use the calculated water equivalent of the apparatus, viz, 2,418.74 grams and 1,980.64 grams, respectively. Taking as an example the first determination in Table 7, we have:

$$2{,}418.74 : (26.24 + 7.10) : : 1 : X$$

$$X = 0.01378° \text{ C.}$$

From Table 7 we learn that 1 gram of the substance (in this case benzoic acid) burned under the normal conditions caused a rise in temperature equal to 2.61101° C. and burned when the water equivalent was reduced by 438.1 grams, caused a rise in temperature of 3.18941° C., the difference being 0.57840° C.

Letting X = water equivalent of the bomb calorimeter, we have

$$2.61101\ X = 3.18941\ (X - 438.1 \text{ grams})$$

$$X = 2{,}415.77 \text{ grams.}$$

Computed according to the first method, the water value of the bomb calorimeter would be 2,415.74 grams, which is practically identical with the foregoing, and 2,415.77 is considered as being the correct water equivalent of this calorimeter and will be used in all computations. It is, of course, the water value at 22.12° C., corresponding to a specific heat of water of 0.99745 (compare p. 20), expressed in terms of mean calories, i. e., of water at specific heat 1.0. It will be seen that this agrees very closely with the value computed from the weights and specific heats of the materials of the calorimeter; hence the latter value used in computing the rise of temperature due to the combustion of the fuse wire and of nitrogen can have introduced no appreciable error.

CORRECTION FOR COMBUSTIBLE GASES IN THE OXYGEN.

Having the water value of the apparatus established, the next step is to test the oxygen supply for impurities in the form of combustible gases, etc. This is very important, for there is in this country at the present time, at least so far as the writer knows, no perfectly pure oxygen put up under high pressure for bomb-calorimeter use, and hence a correction must be worked out for the oxygen used, when accurate work is required. The problem may be established by two different methods:

First, by noting the influence of varying pressure of oxygen upon the combustibility of the gases when the same amount of heat is generated in the bomb during the several combustions.

Secondly, by noting the effect of varying charges, that is, the varying amounts of heat evolved, upon the combustion of the different gases, the oxygen pressure in the bomb being the same.

Analyzed by the copper oxid combustion method, the writer's associate, Mr. Braman, found the oxygen at hand to contain 0.0161 per cent of carbon and 0.0194 per cent of hydrogen by weight, and the question is: Does a part, or all, of these gaseous impurities burn during an energy determination, and, if burned, what will be the rise in temperature caused by the burning?

This bomb charged with 20 atmospheres of oxygen would, according to the above analyses, contain 0.001648 gram of carbon and 0.001986 gram of hydrogen. The ratio of carbon to hydrogen is such that they can not form any one gas, for even should all the carbon be present as methan, there would still be 0.00144 gram of free hydrogen, which alone represents about 50 calories.

It was decided to burn as large a charge of benzoic acid as would possibly burn completely in 10 atmospheres of oxygen, and then burn the same amount in 20 atmospheres; also to burn about half the quantity of the substance in oxygen of the pressures just mentioned. The final results of these tests we desire to express in terms of the quantity of heat generated in the bomb and its effect upon the impurities in the oxygen instead of in terms of any particular substance. But for our immediate purpose, we can express the rise in temperature in terms of the amount of charge used, and hence in the computation of the results we can make use of the newly found water equivalent and follow the same method employed in finding the rise in temperature per gram of substance in Table 7.

Tables 8 and 9 contain the results of two series of combustions of like charges of benzoic acid burned in different amounts of oxygen and the rise in temperature due to the impurities in the oxygen. In the first series of combustions the charges were twice the size of those in the second series. The carbon present in the form of CO_2 in the bomb after a combustion was determined in some instances in the case of the large charges of benzoic acid, and the average of three determinations where 20 atmospheres of oxygen were used was 68.801 per cent of carbon, the theoretical being 68.83 per cent of carbon. The three determinations with the smaller amount of oxygen gave an average of 68.713 per cent of carbon, a difference of about 0.09 per cent. This is an indication that the charges were a little too large, so that with 10 atmospheres of oxygen the combustions can not be relied upon as being complete. Assuming that this small difference in carbon represents the actual difference between complete and incomplete combustion of the benzoic acid, which can not be far wrong, we have a correction which can be applied to the rise in temperature obtained with 10 atmospheres of oxygen.

TABLE 8.—*Rise in temperature caused by burning like quantities of benzoic acid in varying amounts of oxygen. Results corrected for 0.032 gram water evaporation.*

Oxygen pressure.	Benzoic acid burned.	Fuse wire.	HNO_3 formed.	Rise in temperature.[a]	Rise in temperature due to wire and HNO_3.	Rise in temperature due to benzoic acid.	Rise due to 0.7142 gram benzoic acid.
Atmospheres.	*Gram.*	*Calories.*	*Calories.*	*° C.*	*° C.*	*° C.*	*° C.*
20	0.7157	26.24	7.10	1.8915	0.01380	1.87770	1.87377
20	.7341	22.88	7.20	1.9371	.01246	1.92464	1.87247
20	.7034	26.24	6.90	1.8554	.01372	1.84168	1.86996
20	.7162	23.04	6.95	1.8904	.01242	1.87798	1.87274
20	.7110	26.56	6.95	1.8804	.01388	1.86652	1.87492
20	.7045	23.68	6.95	1.8588	.01268	1.84612	1.87154
Average							1.87257
10	.7108	27.04	1.73	1.8708	.01191	1.85889	1.86778
10	.7134	23.36	1.73	1.8752	.01039	1.86481	1.86690
10	.7112	21.12	1.73	1.8615	.00946	1.85204	1.85985
Average							1.86484

[a] Corrected for evaporation and for difference in water value of calorimeter due to differences in amount of oxygen used.

0.7142 gram benzoic acid in 20 atmospheres O_2	1.87257 °C. rise.
.7142 gram benzoic acid in 10 atmospheres O_2	1.86484 °C. rise.
.09 per cent incomplete combustion in 10 atmospheres O_2	.00168 °C. rise.
Difference due to 10 atmospheres oxygen	.00605 °C.

TABLE 9.—*Rise in temperature caused by burning like quantities of benzoic acid in varying amounts of oxygen. Results corrected for 0.032 gram water evaporation.*

Oxygen pressure.	Benzoic acid burned.	Fuse wire.	HNO_3 formed.	Rise in temperature corrected for evaporation and variation in bomb water value.	Rise in temperature due to wire and HNO_3.	Rise in temperature due to benzoic acid.	Rise due to 0.3566 gram benzoic acid.
Atmospheres.	*Gram.*	*Calories.*	*Calories.*	*° C.*	*° C.*	*° C.*	*° C.*
20	0.3648	22.88	3.40	0.9696	0.01088	0.95872	0.93717
20	.3579	21.44	3.40	.9508	.01028	.94052	0.93710
Average							.93714
10	.3595	23.04	1.03	.95245	.01000	.94245	.93484
10	.6301	22.88	1.03	.95215	.00990	.94225	.93309
10	.3585	25.76	1.03	.95315	.01109	.94206	.93707
10	.3484	26.24	1.03	.92385	.01129	.91256	.93404
Average							.93476

0.3566 gram benzoic acid in 20 atmospheres O_2	0.93714 °C. rise.
.3566 gram benzoic acid in 10 atmospheres O_2	.93476 °C. rise.
Difference due to 10 atmospheres O_2	.00238 °C.
Difference due to 15 atmospheres O_2	.00357 °C.

The smaller charges (Table 9) were completely burned in 10 atmospheres of oxygen, which was proved by the carbon dioxid determination after the combustion giving 68.838 per cent of carbon. From the above tables we learn that there was a greater rise in temperature when the combustion took place in oxygen at high pressure than when less oxygen was present. In the case of the smaller charges,

that is, less heat evolution, the difference in rise of temperature was less for each atmosphere difference in pressure than in the case of the greater heat. It is difficult to remove the last traces of a combustible gas from a gas mixture by combustion or electric sparks, and we can not expect that all combustible gases present in the oxygen would be burned in the bomb by a single combustion of any kind of substance. Further, it is to be expected that conditions may be reached relative to dilution of gases, rate of combustion of the substance, and heat evolution when the dilute gases escape combustion altogether. In the case of the 0.7142 gram of benzoic acid burned in 10 atmospheres oxygen pressure, the combustion of the substance was, as stated, not quite complete, that is, vapors or combustible gases from the burning material itself had begun to be left unburned. Hence the point when the combustible gases present in the oxygen supply will practically cease to be affected can not be far either way from 10 atmospheres oxygen pressure, with the larger charge of benzoic acid.

In order to compare the effect of the 0.3566-gram charges upon the combustible gases with that of the larger ones, the resulting rises in temperature are computed to the same basis and are given in Table 10.

TABLE 10.—*Comparison of average results obtained by burning unlike quantities of benzoic acid in like amounts of oxygen.*

Oxygen.	Benzoic acid charges.	Average rise in temperature.	Rise computed on basis of 0.7142 gram charge.
Atmospheres.	*Gram.*	*° C.*	*° C.*
20	0.7142	1.87257	1.87257
20	.3566	.93714	1.87691
Difference			+ .00434
10	.7142	1.86484	1.86652
10	.3566	.93476	1.87214
Difference			+ .00562

Here we notice, first, that the smaller charges show a relatively larger rise in temperature both at 10 and at 20 atmospheres; furthermore, the small charges, which burned completely at 10 atmospheres oxygen pressure, show a greater increase over the large charges at 10 atmospheres than over the same when burned at 20 atmospheres oxygen pressure. This is an indication that the limit for combustion of the gases in the oxygen has not been reached at 10 atmospheres with a small charge. With 0.3566 gram charge, therefore, we can well assume that at 5 atmospheres oxygen pressure the conditions for burning correspond to those at 10 atmospheres with 0.7142 gram charge, i. e., twice the amount, and that, therefore, at 5 atmospheres oxygen the effect upon the combustible gases would have ceased.

Hence, the difference in rise of temperature due to combustible gases present in the oxygen supply when 0.7142 gram benzoic acid is burned in the bomb at 20 atmospheres can be represented by 0.0060° C. as found in Table 8, and for 0.3566 gram charge at 20 atmospheres oxygen 0.0036° C. (Table 9); for other amounts of benzoic acid burned the error due to combustible gases is found by interpolation.

NATURE OF COMBUSTIBLE GASES.

As to the nature of the gas or gases which cause the rise in temperature, we know from the CO_2 determinations that none of the carbon in the oxygen was oxidized, and there remains, therefore, only the free hydrogen, even a portion of which is sufficient to cause the observed rise.

THE HEAT OF COMBUSTION OF BENZOIC ACID.

We now have the correct water equivalent of the calorimeter, a correction for the impurities in the oxygen, and also the evaporation correction, and can proceed to the computation of the heat of combustion of benzoic acid.

In all the determinations the Regnault-Pfaundler formula, referred to earlier in connection with the water value determination by means of electricity, has been used for working out the radiation correction; that is, the correction for the influence of the surrounding air upon the readings. The computation of one of the determinations is given below in detail as an example, and following that will be found tabulated the results of various determinations representing a wide range of conditions, both in regard to quantity of substance burned and oxygen used. It is a satisfactory check upon the accuracy of the bomb work when very different amounts of material are burned and concordant results are obtained.

Example of a determination of heat combustion.

Substance, benzoic acid, Kahlbaum's.
Charge, 0.7157 gram.
Iron fuse wire completely burned, 0.0164 gram=26.24 calories.
Oxygen pressure, 20 atmospheres.
Room temperature, 23° C.
Water temperature before ignition, 21.26° C.
HNO_3 formed and titrated=7.10 calories.
Ignition of charge, instantaneous.
Combustion of substance, complete.
Carbon dioxid found after combustion=68.801 per cent carbon.

Thermometer readings, preliminary	1.438;	1.440;	1.442;	1.444;	1.445.
Thermometer readings, corrected.....	1.4468;				1.4538.
Combustion period readings.....	1.445;	2.920;	3.292;	3.316;	3.317.
Combustion period readings, corrected..	1.4538;	2.9343;	3.3058;	3.3297;	3.3307.
Thermometer readings, end period.....	3.317;	3.313;	3.311;	3.309;	3.308.
Thermometer readings, end period, corrected ..	3.3307;				3.3208.

$$v=0.0018° \text{ C.}$$
$$t=1.4503° \text{ C.}$$
$$\theta=5$$
$$v=-0.0025° \text{ C.}$$
$$t=\ 3.3258° \text{ C.}$$
$$\text{Thermometer lag}=-0.0005° \text{ C.}$$

$$\frac{0.0018-(-0.0025)}{3.3258-1.4503}(11.1959+2.3922-7.2515)-0.0072=+0.0073$$

$$\Sigma\Delta t=+0.0073° \text{ C.}$$

	° C.
Last reading of combustion period	+3.3307
First reading of combustion period	−1.4538
Radiation correction	+ .0073
Correction for thermometer lag	− .0005
Correction for impurities in oxygen	− .0060
Evaporation of water during 4 minutes	+ .0078
Corrected rise in temperature	1.8855
	Calories.
Water value of bomb system with 20 atmospheres oxygen (2415.8) ×1.8855° C	4,554.99
Correction for fuse wire	−26.24
Correction for HNO_3	− 7.10
	4,521.65

4521.65÷0.7157=6317.80 calories per gram benzoic acid.

In like manner all the results found in the following table are worked out:

TABLE 11.—*Heat generated when different quantities of benzoic acid are burned in varying amounts of oxygen, and the heat of combustion per gram of benzoic acid.*

Oxygen pressure.	Benzoic acid burned.	Fuse wire.	HNO_3 formed.	Observed rise in temperature.	Corrected rise in temperature.	Total heat generated in the bomb.	Heat per gram benzoic acid.	Temperature of water before ignition.
Atmospheres.	*Gram.*	*Calories.*	*Calories.*	*° C.*	*° C.*	*Calories.*	*Calories.*	*° C.*
25	0.7088	23.36	8.25	1.8635	1.8655	4,506.75	6,313.68	21.3
20	.7157	26.24	7.10	1.8769	1.8855	4,554.99	6,317.67	21.3
20	.7341	22.88	7.20	1.9288	1.9311	4,665.15	6,313.96	20.8
20	.7034	26.24	6.90	1.8408	1.8494	4,467.79	6,304.73	20.7
20	.7162	23.04	6.95	1.8804	1.8844	4,552.34	6,314.37	21.4
20	.7110	26.56	6.95	1.8653	1.8744	4,528.18	6,321.62	20.9
20	.7045	23.68	6.95	1.8435	1.8528	4,476.00	6,309.97	21.3
15	.7100	26.24	4.40	1.8448	1.86735	4,511.15	6,310.58	20.4
20	.3648	22.88	3.40	.9591	.9660	2,333.67	6,325.07	20.4
20	.3579	21.44	3.40	.9411	.9472	2,288.25	6,324.13	20.3
10	.3595	23.04	1.03	.9431	.95125	2,298.03	6,325.33	19.8
10	.3601	22.88	1.03	.9427	.95095	2,297.31	6,313.24	19.9
10	.3585	25.76	1.03	.9390	.95195	2,299.73	6,340.13	20.5
10	.3484	26.24	1.03	.9095	.92265	2,228.95	6,319.38	20.7
Average							6,318.12	20.7

In the above table representing fourteen determinations made under such varied conditions the results agree very well; for if we leave out the two extreme results the greatest difference from the average in the remaining twelve determinations is but 8.15 calories. Computed by the usual formula, the probable error of the mean of the

fourteen determinations is ±1.51 calories and the probable error of a single determination ±5.69 calories.

SULPHUR, PHOSPHORUS, AND CHLORIN.

The writer sometime ago[a] called attention to the fact that the acid found in the bomb after a combustion is not always HNO_3 alone, and that it is especially the S in organic combination, which goes over into gaseous SO_3 and eventually into H_2SO_4, that needs to be considered. Hence the sulphuric, phosphoric, and hydrochloric acids are determined when found in sufficient quantities, and the total acidity found by titration is correspondingly corrected in computing the heat arising from the oxidation of free nitrogen. Determinations of sulphur and phosphorus have been successfully carried on in feeds, feces, and urines by the bomb method during these last three years in this laboratory. In the two samples of benzoic acid which were used in the above determinations, one, Kahlbaum's best, gave no test for Cl. and only a light trace of SO_3. The other sample, "Merck," gave but a small trace of SO_3 and a distinct trace of Cl., but in no case enough to be determined for the sake of correction.

CORRECTION FOR THE SPECIFIC HEAT OF WATER.

Since the specific heat of water differs at different temperatures, the water equivalent of the calorimeter will also vary with the temperature. In the above case the water equivalent was determined with an average of 21.08° C. water temperature before the combustions and an average of 23.15° after the combustions. The mean specific heat between these temperatures is 0.99745. The mean specific heat between the average temperatures before and after combustions in the fourteen determinations of Table 11 is 0.99752.

The true average heat of combustion, therefore, is

$$6{,}318.12 \times \frac{99752}{99745} = 6{,}318.56 \text{ calories.}^{b}$$

CHANGE IN THE BOMB CONTENTS.

There are at least two other conditions which should be considered, since they may to some small degree influence the heat of combustion as computed from the determinations already described and recorded in Table 11.

One is a possible change in the water value of the calorimeter which may be caused by the combustion of the substance in the bomb. According to the nature of the substance, the contents of

[a] U. S. Department of Agriculture, Bureau of Animal Industry Bulletin 94, p. 32.

[b] This method of computation assumes, of course, that the specific heats of the materials of the calorimeter itself vary with the temperature at the same rate as does that of water. The total correction is so small, however, that any error thus introduced must be insignificant.

the bomb will change more or less, so as to make the water equivalent after the combustion different from what it was before.

When the same kind of material is burned as that which was used for the determination of the water value of the bomb, the changes need not be considered except when a different quantity is burned. Should an entirely different compound be burned, even if in a quantity like that used for water value determinations, the condition existing in the bomb before and after combustion should be computed whenever it is possible to do so, in order to determine whether enough change took place in the water equivalent of the bomb to call for a correction. In the computations we use the following values:

Volume of gas in bomb at 20 atmospheres, measured at 20° C., 730 mm. pressure,[a] is 8 liters.

	Grams.
Weight per liter O_2 at 20°, 730 mm	1.2798
Specific heat O_2, constant volume	.157
Specific heat, CO_2, constant volume	.149
Specific heat benzoic acid, computed	.30
Specific heat Fe_3O_4	.167
Specific heat Fe_2	.1114
Specific heat HNO_3	.445
Specific heat H_2O	1.0000

The average of 10 charges used in the water value determinations equals 0.7102 gram benzoic acid, and considering all the gas as oxygen we have in the bomb before the combustion the following water equivalent:

	Grams H_2O.
Benzoic acid, 0.7102 gram×0.30	0.2131
Oxygen, 8×1.2798×0.157	1.6074
Iron wire, 0.0164×0.1114	.0018
Total	1.8223

After the combustion there are in the bomb the following substances:

	Grams.
Carbon dioxid, 0.7102×2.5246	1.7930
Water, 0.7102×0.4426	.3143
Fe_3O_4, 0.0164×1.381	.0227
Oxygen, 10.2384−1.4309	8.8075
N_2O_5	.0275

This is equivalent to the following amounts of H_2O:

	Grams H_2O.
1.7930 grams CO_2×0.149	0.2672
.3143 gram H_2O×1.000	.3143
.0227 gram Fe_3O_4×0.167	.0039
.0321 gram HNO_3×0.445−0.0046	.0097
8.8075 grams O_2×0.157	1.3828
Total	1.9779

Thus with benzoic acid there is a change of only about 0.16 gram water equivalent caused by the combustion.

[a] Average for this locality.

If instead of benzoic acid, 0.7 gram of ethyl alcohol were burned, we should find a difference of about 0.39 gram water equivalent caused by the combustion and about 0.44 gram water equivalent different from that obtained by benzoic acid. The average charge in the fourteen determinations of Table 11 equals 0.5609 gram, and the average charge used in standardizing the bomb was 0.7102 gram, which is equivalent to a difference of 0.08 gram in the water value of the bomb, or a correction of −0.20 calorie per gram in the average result. This is a very small correction and usually need not be considered at all.

CHANGE OF PRESSURE IN THE BOMB.

The second condition referred to above is the change in pressure in the bomb resulting from the combustion. By the heat of combustion of a substance is generally understood the heat at constant pressure, which is in many instances slightly different from that determined by the bomb calorimeter at constant volume. Since it is the difference between the conditions before and after the combustion which is considered, it makes no difference what pressure the gases may be under in the bomb before the combustion. If the pressure of the gases before and after the combustion remains the same, the heat of combustion at constant volume and constant pressure is the same. Leaving out of account the small changes due to the oxidation of iron and the formation of nitric acid in the bomb, this is theoretically true of carbohydrates where CO_2 and O_2 replace each other volume for volume. With other substances it may be different. At constant pressure compounds containing much hydrogen will cause a decrease in volume of the gases and hence require a plus correction, and compounds with less hydrogen but plenty of nitrogen may cause an increase in gas volume, and consequently there will be a minus correction to the results obtained by the bomb.

For a solid or liquid substance of the composition $C_nH_pO_q$ burned at constant volume in the bomb the heat at constant pressure is expressed by the following formula:[a]

$$CtP = CtV + 0.5424\left(\frac{\frac{1}{2}p - q}{2}\right) + 0.002\left(\frac{\frac{1}{2}p - q}{2}\right)t$$

where

t = temperature.

p and q = number of atoms in the molecule.

According to this formula, benzoic acid, $C_7H_6O_2$, at constant pressure will be:

$$CtP = CtV + 0.5424 \times \frac{3-2}{2} + 0.002 \times \frac{3-2}{2} \times 22.8°$$

which expressed in calories per gram equals:

6,318.56 + 2.41 = 6,320.97 per gram benzoic acid.

[a] Beilage zum Chemiker-Kalender, 1904, p. 144.

If to this we apply the correction found for the change in the bomb content because of unlike charges, -0.20 calorie, the heat of combustion of 1 gram benzoic acid, $C_7H_6O_2$, at constant pressure will be: $6{,}320.77 \pm 1.51$ mean calories, a value practically identical with that found by Stohman, viz, 6,322 calories.

USE OF THE BOMB CALORIMETER UNDER DIFFERENT CONDITIONS.

Judging from these investigations, there are many conditions which may influence the work with the bomb and cause the results to become inaccurate, and the question is, What is the best and most convenient way to operate the bomb so as to get reliable results under the various conditions? Three methods in regard to the determination of the water value of the calorimeter and its use may be employed according to existing laboratory and other conditions:

1. The apparent water value may be directly determined by burning a given weight of a standard substance, note being taken of all the conditions existing at the time of standardization of the bomb, including amount of substance and of oxygen, and atmospheric conditions influencing evaporation. If, now, the substance to be analyzed corresponds in quantity to the calories generated at the standardization, and if the other conditions are the same, there will be no corrections to apply for impurity in oxygen or for evaporation of water. Whether the small correction for constant volume and for change in contents of the bomb need to be applied depends upon the degree of accuracy to which the operator expects to work.

2. Should it be required to burn charges giving much more or less heat than that used for standardization, with the oxygen supply and evaporation condition remaining unchanged, then it is most convenient to have the water value of the bomb determined with the smaller or larger charges also, and thus avoid the use of corrections.

3. When, however, the heat determinations must be made under varying temperature conditions, with different amounts of substance and various oxygen supplies, then all the corrections due to variation from the conditions at which the bomb was standardized must be applied.

The different water values for the bomb calorimeter used in this work corresponding to the above three methods of usage would be, including 2,000 grams of water:

Method 1, with 0.7142 gram benzoic acid charge, 2,421 water value.

Method 2, with 0.3614 gram benzoic acid charge, 2,425.4 water value.

Method 3, with 0.7102 gram benzoic acid charge, 2,415.7 water value.

In the third or last value, the corrections due to evaporation of water and specific heat of water have been applied.

CORRECTIONS FOR IMPURITIES IN OXYGEN.

Having now the specific heat of combustion of benzoic acid, we can find from Tables 8 and 9 the correction for impurities in the oxygen expressed in degrees rise of temperature, or its equivalent in calories, for any given amount of heat generated in the bomb during a combustion. All substances do not affect the combustible gases alike, but for this purpose we may assume benzoic acid to be a representative substance, and each kind of material need not be tested separately. The average of six charges of benzoic acid was 0.7142 gram, which, multiplied by 6,320.8 equals 4,514.3 calories. This amount of heat caused a rise in temperature of 1.87257° C. with 20 atmospheres oxygen, and with 10 atmospheres oxygen a rise of 1.86652° C., a difference of 0.00605° C., which is equal to 14.62 calories. In like manner, the average charge, 0.3566 grams benzoic acid, Table 9, equals 2,254 calories and causes a total difference of 0.00357° C. rise, equivalent to 8.59 calories.

By interpolation we have, according to the various amounts of heat generated in 20 atmospheres oxygen pressure, the corrections for the oxygen shown in Table 12. They are applicable, of course, only to the particular sample of oxygen used in these determinations, and unless a uniform quality of the oxygen in this respect can be assured, it would be necessary to redetermine their factors for each cylinder of oxygen.

TABLE 12.—*Corrections for combustible gases in oxygen.*

Heat generated in bomb.	Correction in terms of—	
	Rise of temperature.	Calories.
Calories.	° *C.*	
4,500	0.00603	14.55
4,000	0.00550	13.22
3,500	0.00495	11.89
3,000	0.00440	10.57
2,500	0.00385	9.24
2,250	0.00357	8.58
2,000	0.00330	7.91

BENZOIC ACID AS A STANDARD.

From his experience with various substances, and because of the value obtained for benzoic acid as described in this paper, the author in conclusion urges all persons using the bomb calorimeter for scientific work where results are to be published, for the sake of uniformity and comparability of results, to adopt benzoic acid as the one single standard against which to standardize the bomb, and to accept 6,322 calories per gram as its heat of combustion. This is the value accredited to Stohlmann, and this value ought to remain the standard until it has been definitely proved to be erroneous and a new value in some way officially recognized or accepted.

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